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A Review of the Catalytic Effects of Lead-Based Ballistic Modifiers on the Combustion Chemistry of Double Base Propellants

Lisette R. Warren,^[a] Zixuan Wang,^[a] Colin R. Pulham,^[a] and Carole A. Morrison^{*[a]}

Abstract: Lead-based compounds are the current industry-standard ballistic modifier for double-base propellants, but there is a pressing need for alternatives as incoming European legislation will soon ban their use. This review article introduces the main concepts and terminologies in the combustion chemistry of double-base propellants, and critically evaluates the four theories put forward in the liter-

ature to account for the ballistic modifier effect, namely (i) photochemical, (ii) chelating/complex, (iii) carbon soot, and (iv) free radical theories. We also review the literature on current trends in ballistic modifier research and note the emerging potential of oxide nanoparticles (in particular Bi_2WO_6) and Cu/Bi encapsulated in carbon nanotubes as lead-free ballistic modifier additives.

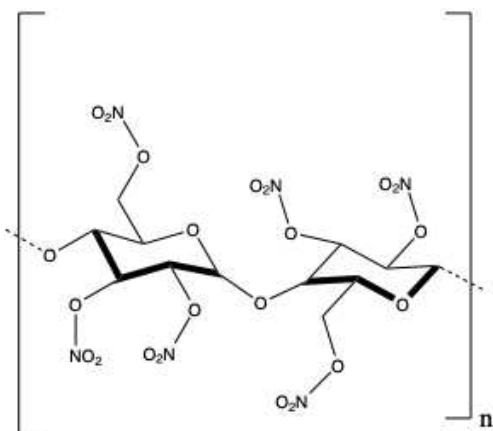
Keywords: Double base propellants • Lead-based ballistics modifiers • Review

Introduction

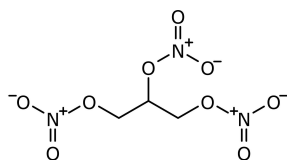
Solid propellants are mixtures containing both oxidisers and fuels, which can burn in low air environments to produce large volumes of smokeless gas [1]. One class of solid homogenous propellants are the double base propellants

(DBPs), which are commonly based on nitrate esters. The first formulation can be traced back to 1887 when Alfred Nobel patented ballistite, which was based on nitrocellulose (NC, Scheme 1) plasticised by nitroglycerin (NG, Scheme 2) [2]. Since then, many developments have ensued, mainly directed at improving the stability and reliability of DBPs; typical compositions are comprised of nitrocellulose (40–70%) and nitroglycerin (15–41%), along with various additives to improve chemical stability and burn rate properties. Presently, DBPs are used for the launch systems of rockets, mainly because of their greater safety and reliability in comparison with liquid fuels [1], while their smokeless attributes also lend them to applications in gun and mortar propellants [3,4].

A prerequisite feature for solid propellants is that the products of their combustion are almost all gaseous substances at high temperatures, with a boiling point range of $T_b = 2500\text{--}3900\text{ K}$ [5]; this acts to provide the desired propulsion for the projectile. The high material density of solid propellants leads to a high energy density (*i.e.* the energy



Scheme 1. Chemical structure of fully nitrated cellulose (nitrocellulose), 14.14% N by weight.



Scheme 2. Chemical structure of nitroglycerin.

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produced by a unit mass of propellant), which can be as high as 10^6 W cm^{-3} [6].

There are two important features of solid rocket propellants: the specific impulse I_{sp} and the burn rate r . The former is defined as:

$$I_{sp} = k_1 \cdot (T_c N)^{0.5} = k_2 \cdot (T_c M)^{0.5}$$

Where T_c is the combustion chamber temperature, N is the number of molecules per unit weight, M is the mean molecular weight of the combustion gases, and k_1 and k_2 are rate constants. Thus, high values of I_{sp} are obtained for high chamber temperatures and low weights of reaction products. Typically, DBP I_{sp} values range from 2100 to 2300 N s kg^{-1} [7]. The burning rate characteristics are related through Vieille's Law:

$$r = a \cdot p^n$$

Where a is the burn rate constant, p is the combustion chamber pressure, and n is the pressure exponent. In the presence of burn rate catalysts, typical pressure exponents n range from 0 to 0.3, with a burn rate of 10–25 mm s^{-1} at 7 MPa [7].

With the aim of achieving better control of the burning rate of DBPs, researchers have long been focusing on adding catalysts, typically lead-based compounds, into DBP formulations. This development dates back to World War Two when researchers serendipitously discovered that the use of lead compounds as lubricants in the propellant manufacturing process had modified their burning characteristics [8]. These additives termed ballistic modifiers, or burn-rate catalysts should impart multiple properties, namely (i) burn rate acceleration (called "super-rate" burning) at a low (ambient) pressure range, followed by (ii) a levelling off of the burn rate (the "plateau effect", due to a loss of catalytic effect) at intermediate to high gas pressures, or sometimes a negative exponent ("mesa" burning), followed by (iii) a return of the burning rate towards that of a non-catalyzed propellant (see Figure 1)) [9]. The pressure exponent n is ideally zero for plateau burning (accepted values lie in the range 0 to 0.3) and negative for mesa burning. Plateau and mesa burning characteristics are in effect insensitive to changes in pressure [3,9].

An investigation into the effects of metal oxides as ballistic modifiers showed that the burning rates of propellants containing Fe_2O_3 , Co_2O_3 , CuO , ZnO , SnO_2 , and Al_2O_3 increased linearly with pressure, i.e., super-rate burning, but that no plateau or mesa burning occurred at high pressure; Pb-based compounds were the only metal oxides to produce all three burning effects [10]. This continued reliance on Pb-based ballistic modifiers is problematic due to its inherent toxicity [11], and impending European legislation will place a ban on its use [12,13]. Alternatives that offer the same performance credentials have yet to be identified.

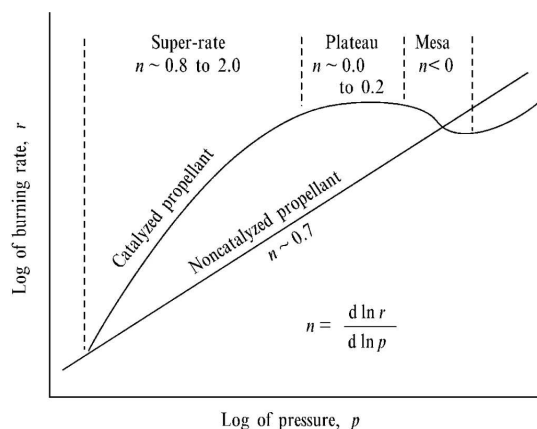


Figure 1. Burning rate-pressure relation for non-catalysed and catalysed DBP [9]. Copyright (1974) AIAA.

Possible mechanisms to account for the observed behaviour of lead-based ballistic modifiers have been proposed in the literature from the 1950s until the early 1990s. Consensus has been reached on some aspects, but disputes and uncertainties on others persist, especially on the mechanism of inducing the plateau and mesa burn rate effects. Theories on catalytic mechanisms also vary, and thus the purpose of this review is to compare and classify the existing knowledge into four categories, according to their proposed chemical reaction mechanisms. These are (i) the photochemical theory, (ii) the chelating theory, (iii) the carbon soot theory and finally (iv) the free radical theory. Critical evaluations of each will be covered in the upcoming section, following a brief introduction into the combustion chemistry of DBPs. We then end with a brief review of the current trends in ballistic modifier research in DBPs.

Combustion Reactions and the Five Combustion Zones

To account for both the super-rate burning and the plateau/mesa burn-rate effect behaviours, the proposed chemistry on the decomposition of nitrate esters must be critically examined. To this end, references covering a brief introduction into the combustion chemistry of DBPs, as well as the terminologies used, are briefly discussed here.

The combustion wave of a double-base propellant consists of five successive zones, as shown in Figure 2. They are: (i) the condensed phase conductive heat zone, (ii) the foam zone (also referred to as the burning surface), (iii) the fizz zone (also called the primary flame zone), (iv) the dark zone, and finally (v) the flame zone (also known as the secondary flame or luminous flame zone) [14–19]. The chemical reactions taking place at each combustion zone are also illustrated in Figure 2, and the narrative presented here follows the discussion by Fifer [19] and Lengellé et al. [18]. It is thought that no reactions take place in the conductive heat

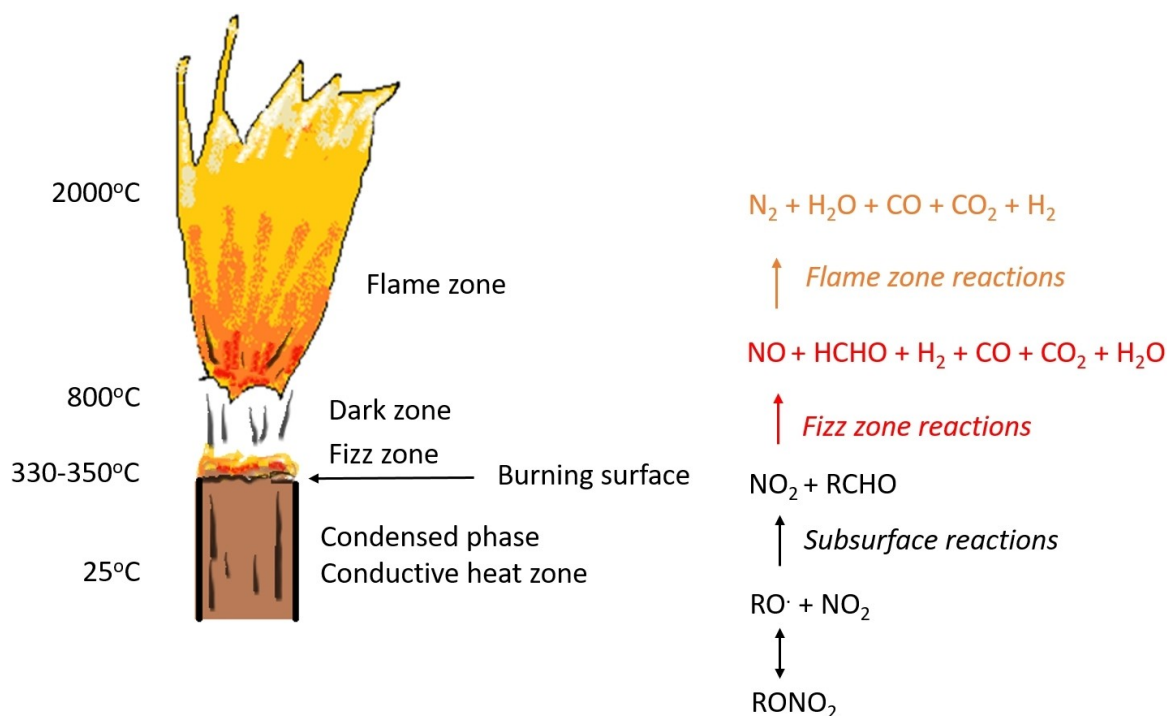


Figure 2. Combustion wave structure and chemical reactions within each combustion zones of DBPs.

zone and that the temperature increases until the propellant components reach the foam zone, just below the burning surface. Here the temperature is high enough for thermal degradation to be significant, initiating the breaking of the $RO-NO_2$ bond, to produce alkoxy and nitro radicals. Activation energies are approximately 160 kJ mol^{-1} , an energy which can be associated with this bond breaking event [18,20,21]. This step is a reversible reaction (due to the low mobility of these products in the solid phase), whose direction is readily tuned through stoichiometric factors [19,20]. Further evidence for the reversibility of this reaction is apparent from the observation that nitrate ester decomposition is hindered when NO_2 is added [19,20], a phenomenon also noted for other simpler mononitrate esters [22–27], and in an elegant study by Hiskey et al. [22] where NO_2 and alkoxy radicals were trapped in close proximity by solvent viscosity. After production of the radicals [23,24], simultaneous secondary reactions occur at the burning surface. Experimentally, it is very difficult to sample the gaseous products of the condensed phase reactions, but careful analysis under vacuum has detected large volumes of NO_2 [18–20,28] and aldehyde fragments [18]. Overall the processes at the foam zone are exothermic [18,19,29]. Thermocouple measurements have attempted to measure the temperature of the thin burning surface and suggest temperatures of uncatalyzed DBPs are of the order of 300°C and do not exceed 500°C [21].

The gaseous products formed at the burning surface then diffuse into the fizz zone, where exothermic processes

take place and the temperature rapidly increases [18]. Combustion products formed in this zone depend on the initial ratios of the propellant (*i.e.* the nitration levels of nitrocellulose and the ratio of NC/NG), but in general, a mixture of oxidation and reduction processes occur to produce the major products NO and CO , and smaller amounts of the final combustion products CO_2 and H_2O . H_2 and carbonaceous materials also form here [18,19]. The dark zone functions as a transition phase between the fizz zone and the flame zone, and it is unclear what redox reactions occur here. This is primarily because detection of gaseous products in the fizz zone are measured through the dark zone [18,28], and in final combustion analysis when no luminous flame exists [19]. In general, reactions in the dark zone are thought to involve the slow reduction of NO to N_2 , until the temperature and pressure are high enough to form the luminous flame zone. The primary processes occurring in the flame zone is the reduction of NO to N_2 , and oxidation of CO and H_2 to CO_2 and H_2O , respectively. At low pressures, the luminous flame zone is non-existent but predominates over the dark zone at higher pressures [14,30].

The following sections are dedicated to a discussion on the catalytic theories put forward to account for the super-rate and plateau-/mesa-burning rate effects induced by lead-based ballistic modifiers.

Lead Catalysis of DBPs: Super-Rate Burning and Plateau/Mesa Effect Theories

A number of papers report on the detection of possible intermediate products in the combustion of DBPs in the presence of lead catalysts, and to propose potential mechanisms to account for their super-rate and plateau/mesa effect properties. A summary of the broad headlines is presented in Table 1; each theory will be critically evaluated in turn, and the commonalities between them discussed.

To understand how a lead catalyst influences the burning rate of DBPs, a number of factors must be ascertained. The active form of lead must be identified, along with the reaction(s) it influences. This is likely to involve reaching an understanding on how the catalyst influences the equilibria in nitrate ester thermal decomposition. In addition, conditions operating in the reaction phase (*i.e.* at the burning

surface, the fizz zone and beyond), where the catalysts operate, must also be understood. All three concepts must, therefore, be discussed for the competing theories outlined in Table 1.

Photochemical theory. According to the theory by Camp et al. [31,32] the increase in DBP burn rate is due to a photochemical enhancement of nitrate ester decomposition near the burning surface and in the condensed phase sub-surface zones. The radiation in the luminous flame zone is enhanced by metallic lead radiation emission, due to the presence of lead metal vapours in the flame. This, in turn, further enhances the decomposition of nitrate esters at the burning surface (see Figure 3). The plateau and mesa effects arise due to physical blockage of UV radiation reaching the burning surface due to lead metal accumulation at high gas pressures. Accumulation of metallic lead at the burning sur-

Table 1. Classifications of catalytic theories on combustion of DBPs and key ideas toward super-rate phenomenon and plateau/mesa effect respectively.

Theory classifications	Representative researchers	Super-rate mechanism	Plateau/mesa effect mechanism
Photochemical theory	Camp et al. [31,32]	Lead catalyst promotes absorption of radiation below the burning surface, which is the significant factor for burning rate acceleration.	Lead droplets cover solid reaction surface as pressure increases, hindering absorption of radiation.
Chelating/complex theory	Suh et al. [33]; Farber et al. [28]; Fifer et al. [34]; Tajima et al. [35]	Lead and combustion product NO_2 form physio-sorbed complexes, pushing reversible combustion reactions forward.	No explanation offered.
Carbon soot theory	Youfang [36]; Kubota [29,37]; Hewkin et al. [10]; Lengellé et al. [21].	Lead catalyst promotes formation of soot on burning DBPs, which in turn catalyses reduction of NO .	Carbon is removed due to oxidation by NO as fast as it is produced.
Free radical theory	Sinha et al. [38]	Alkyl radicals in condensed phase complex as lead alkyls, which decompose in the fizz zone and chain react with NO .	Increase in pressure promotes free radical collisions, forming plateau burning.

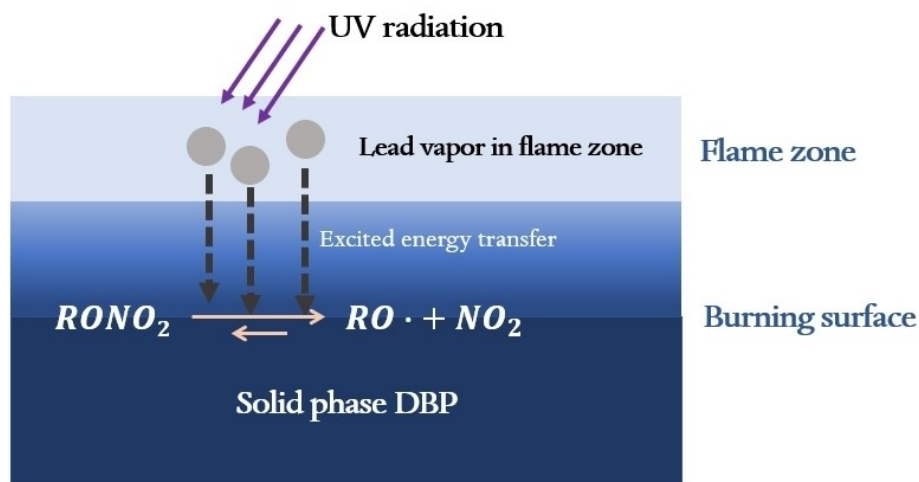


Figure 3. Photochemical catalysis theory of super-rate enhancement mechanism of DBP combustion.

face has also been observed by Farber et al. [28] and Hewkin et al. [10]

Several problems exist with this theory, however. If super-rate burning was due to high UV radiation absorption from the luminous flame zone, the ballistic modifiers could not be expected to produce any catalytic effect at the low pressure domain [17], where a luminous flame either does not exist or is very weak, and thus the plateau/mesa effect should prevail. This point is substantiated by Kubota et al. [29], who found that the luminous flame disappeared below 7 kg cm^{-2} pressure, but super-rate burning persisted above this threshold. While studying the effect of UV light on the burning rate, Kubota et al. [29] detected that UV light itself did not contribute particularly to burning rate enhancement. As it is known that cellulose-based nitrate plastics can be protected against UV radiation by shielding them with UV absorbers like 2,2'-4,4'-tetrahydroxy benzophenone (THB) [39], Rao et al. [30] studied the effect of adding THB into the lead methylene disalicylate (LMDS) DBP formulation. Relevant results are summarised here in Table 2; from this, it is apparent that the presence of THB does not affect the catalytic performance of LMDS, as evidenced by the high burning rates of propellants containing a mixture of both THB and LMDS. Therefore, these experimental findings do not lend support to the photochemical theory.

Chelating/complex theory. The primary concept behind this theory is that lead salts modify the initial decomposition of nitrate esters through complex formation. As this occurs in the condensed phase, all theories proposed here deduce that catalysis must occur at or near the burning surface. This theory was initiated by Dauerman and Tajima, [35] who studied the decomposition of NC, in isolation and the presence of a 2% lead stearate additive. They proposed that any NO_2 that forms would immediately complex in nitrocellulose, thus pushing the reversible decomposition of nitrate ester forward, which would then decompose very rapidly to form highly oxidised species such as CO , CO_2 , H_2O and some intermediate species.

Following this, Suh et al. [33] proposed the formation of chelated complexes between lead and nitro oxygen atoms

on nitrocellulose, which act to alter the initial decomposition of RO-NO_2 bonds. The action of lead catalysts at or near the burning surface is in support of the work of Kubota et al. [29]. Experimentally, an increase in temperature is observed just above and below the burning surface of the modified propellant (compared to uncatalyzed DBP), which is particularly evident at low pressures [33]. The formation of the chelated complex is thus thought to cause the low-pressure super-rate effect. Further support comes from the observation that tetraphenyl lead does not act as a burn rate catalyst [33]. However, this theory only accounts for super-rate burning. No explanation is proposed to account for the important plateau burning characteristics. A further potential issue with the chelating theory is the fact that non-chelate forming lead compounds, such as lead oxides (PbO , PbO_2 , etc.), also demonstrate catalytic effects [36,40].

Fifer and Lannon [34] instead proposed formation of a π -bonded complex between PbO and secondary products in the condensed foam zone of DBPs. Their idea originates from the work of Salooja [41], who found that lead oxide inhibits the combustion of hydrocarbons, but strongly promotes the combustion of oxygen derivatives of hydrocarbons (e.g. methanol, formaldehyde, methyl acetate etc). In Salooja's paper, this argument was used to account for the reduction of PbO to Pb , and the formation of large amounts of CO_2 and CO [41]. The lead (an inactive catalyst) can be reoxidised to PbO by oxygen-containing radicals. In the context of DBPs, this also accounts for higher ratios of CO_2/CO in leaded propellants as seen by Fifer and Lannon [34]. It also explains why lead halides do not act as catalysts, as they cannot decompose to PbO , whilst almost all lead salts can thermally decompose to PbO [34].

In 1978, Farber et al. [28] conducted a mass spectrometry study of DBPs matrices that contain lead organic salts. Their results revealed that the lead salts do not vaporise, but instead decompose to gas phase metallic elements under combustion conditions. Notably, they show that tetraphenyl lead does not thermally decompose, and may provide insight into its lack of catalysis as discussed by Suh et al. [33]. Thus, the work of Farber et al. does not support the chelate theory of Suh et al. Instead, Farber et al. [28] propose that free lead atoms are responsible for catalysing the nitrate ester decomposition reactions. They point towards formation of PbNO_2 , which is stable in the intermediate temperature zones. Their data also suggests the formation of hydrocarbons and NO_2 at the burning surface, prior to formation of the flame zone.

Support for a complex between a catalyst and NO_2 species comes from the initial work of Levy, who studied the thermal decomposition of simple mononitrate esters [23,42]. Levy showed through infrared studies that the formation of nitrile esters was possible through the decomposition mechanism of nitrate esters. The alkoxy radical produced by reaction (1) has the ability to recombine with NO_2 to give the nitrate ester, fragment to produce ethyl radicals and formaldehyde in reaction (2), or react with NO

Table 2. Effect of UV absorber THB on the burning rates of DBPs, in the presence and absence of lead methylene disalicylate (LMDS). Taken from Ref. [31].

Additives	Burning rates (mm/s) at pressures (kg/cm ²)			
	35	50	70	105
THB (2 parts per 100 parts)	5.2	6.5	8.0	10.2
THB (2 parts per 100 parts) + LMDS (2 parts per 100 parts)	8.8	11.4	13.5	15.7

(produced by reduction of NO_2) in reaction (3). Importantly, nitrile esters decompose approximately 3.25 times slower than nitrate esters. So, if a burn rate catalyst can complex in some way with the NO_2 radical, it would prevent both the reverse reaction of Equation (1), while promoting the formation of the slowly decomposing nitrile ester in Equation (3).



Notably, whilst Levy's work is a model for nitrate esters, in that it only considers the thermal decomposition of ethyl nitrate, the reversible dissociation of nitrate esters in Equation (1) has been extended to more complex nitrate esters like nitroglycerin [43].

With regards to the work of Farber et al., if metallic lead reacts with the NO_2 produced by Equation (1), the product PbNO_2 is formed (Equation 4). This species was observed by Farber et al. [28]. The reversibility of Equation (4) is intended to show that the complex formed is a weak complex, and can back dissociate to Pb and NO_2 . This dissociation frees NO_2 to initiate the heat-producing oxidation reactions to NO and finally to N_2 . However, the formation of the complex disrupts the decomposition pathway, allowing NO_2 to temporarily escape from the alkoxy radical, preventing the reverse reaction of Equation (1), as well as the nitrile formation in Equation (3). We note that Farber et al. [28] identified PbO , Pb_3O_4 and PbO_2 as combustion products in their mass spectrometry investigation, leaving the possibility that these species could also be acting in a catalytic capacity. Moreover, the work of Farber et al. only accounts for super-rate burning and does not propose a mechanism for plateau burning.



The residing similarities between these studies is that some catalysis from Pb salts takes place in the condensed phase, altering the reaction pathways beneath the burning surface [28,33]. Apart from the π -bonding complex theory, there is a common theme of tying up the nitro group moiety, which would accelerate the initial dissociation of the $\text{RO}-\text{NO}_2$ bond. Finally, note that while offering plausible explanations for the super-rate burning, this theory cannot account for the decrease in burn rate observed during the plateau and mesa regions, and thus overall offers only a partial interpretation of ballistic modifier action in the burning of DBPs.

Carbon soot theory. Arguably the leading voice on the combustion chemistry of DBPs, Kubota and co-workers have rationalised catalytic super-rate burning schemes in a series of papers [9,17,29,37]. They have found that the

presence of lead salts is accompanied by a large amount of particulate emission from the burning surface and that these particles expand over a large distance in the flame. In 1991, Sharma et al. [44] presented direct proof, using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX), that the glowing particles emerging from the propellant burning surface were largely fluffy carbon soot particles finely dispersed with lead (see Figure 4).

Kubota et al. [29], therefore, hypothesised that the burning rate enhancement offered by lead compounds is a result of acceleration of the fizz zone reactions, which leads to super-rate burning due to increased heat conduction to the surface. This was accompanied by higher surface temperatures in catalysed propellants, but no change in the end temperature of the fizz zone [29]. They proposed that the acceleration of the fizz zone reactions was due to a decrease in the RCHO , NO_2 stoichiometry in the presence of lead compounds, which in turn was due to increased production of carbon soot at the burning surface. This mechanism, as shown below in Figure 5, presents the idea that the lead catalysts alter the pathways of the secondary reactions at the burning surface, favouring formation of carbonaceous materials over aldehyde fragments.

Rather compellingly, a simplified mathematical model of Kubota's hypothesis was also developed and showed that a shift in the underlying reaction kinetics from a single reaction pathway toward a second, more reactive pathway (i.e. involving the carbon soot) would result in a pressure-dependent super-burn rate and that the rate of burning would drop as the pressure increased. A further release in

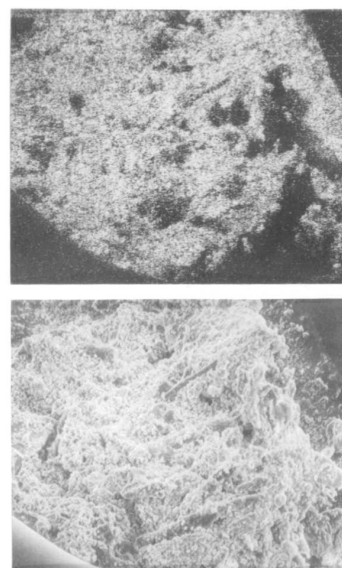


Figure 4. EDAX map (top) and SEM micrograph (bottom) of the same area of soot collected from the surface of catalysed DBP extinguished at 8 MPa pressure. The EDAX map for lead shows that lead is uniformly and finely dispersed in the soot [44]. Copyright (1991) Published by Elsevier Inc.

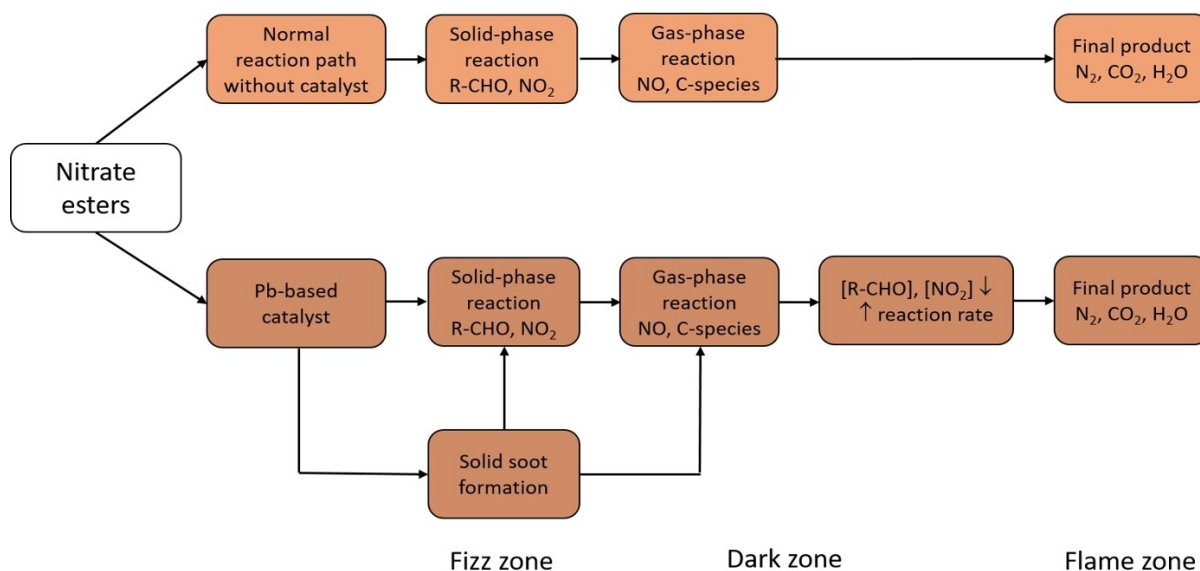
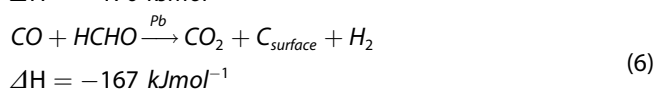
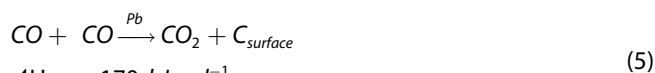


Figure 5. Additional reaction pathway in mechanism for super-rate burning proposed by Kubota [29].

the series by Kubota [37] extended this mechanism to plateau burning, where the conductive head feedback to the burning surface is constant in the plateau burning region. Thus, the burning rate behaviour is dependent on the heat transfer from the fizz zone back to the propellant burning surface. In this way, Kubota's hypothesis appears to successfully quantify all three stages of DBP ballistic modifier behaviour [9, 17, 29, 37].

Another huge contribution in this field comes from Hewkin et al. [10], who investigated many lead compounds as burn rate catalysts, and showed that they primarily affect the formation of the carbonaceous matter near the burning surface. Hewkin et al. [10] thus proposed that the catalytic species consisted of a fine lattice of carbonaceous material, with an accumulation of Pb species dispersed on top, formed within the solid phase reaction zone. Fifer and Lannon [34] speculated that any simple reaction involving the formation of solid carbon would be exothermic and thus increase the burn rate:



However, their work does not mention the form of the Pb catalyst and only accounts for super-rate burning [34].

The work by Hewkin et al. [10], through increased detection of N_2 (and reduction of NO) across a variety of sim-

ple nitrate esters in the presence of lead compounds, deduced that the burn rate enhancement is due to an increased reduction of NO to N_2 . The elevated temperatures from catalysis near the burning surface not only activate the surface carbon but also appear to promote its formation. It should be noted, however, that even though the authors proposed the catalytic reaction occurs in the fizz zone with a Pb/C complex, no strong decrease in NO (or increase in N_2) is observed directly for DBPs.

Evidence from SEM imaging by Kubota et al. [29] and Hewkin et al. [10] provided proof that carbon formation is induced in the presence of lead salts. The carbonaceous matter forms as thin filaments in the burning surface zone (see Figure 6) which can flake off and pass through into the fizz zone. However, even though both groups found evidence for the formation of a lead-carbon complex at the

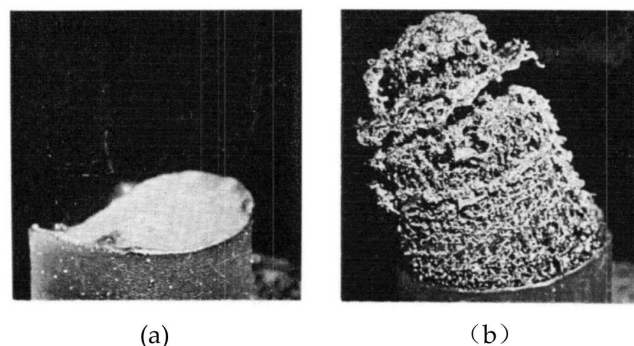


Figure 6. SEM microscopy of (a) Carbon soot formation induced by lead on the burning surface of cellulose based DBP; (b) Peeling off of carbon soot in layers during combustion [10]. Copyright (1971) Published by Taylor & Francis.

burning surface, they disagree on how this affects the decomposition of nitroglycerin. Kubota et al. [29] believe that lead salts affect the secondary reactions at the burning surface, thus increasing carbon formation over the formation of aldehyde species, whereas Hewkin et al. [10] postulated that the lead-carbon matrix catalysed NO to N₂ in the fizz zone, which would otherwise occur slowly in the dark zone.

In 1987 Youfang [36] wrote a new compelling theory which contributes further to the carbon soot theory. Youfang [36] postulated that lead salts decompose into PbO, which has high thermal stability. Following this, PbO acts as a catalyst to alter the decomposition products of aldehyde fragments formed at the burning surface, promoting formation of carbonaceous matter onto the lead monoxide particles. This results in carbon nuclei that rapidly nucleate to form a carbonaceous layer. Experimental evidence for this theory is derived from Hewkin et al., [10] where PbO added directly as an additive promoted decomposition of para-formaldehyde into carbon at 180°C. Lengellé et al. also agree with the formation of a PbO/C complex, but they discuss that lead salt degradation would not occur until the fizz zone (within the carbon residue), leaving the condensed phase reactions uncatalyzed [21].

In agreement with Hewkin et al., [10] Youfang's theory [36] states that the presence of carbon soot on the burning surface promotes the reduction of NO to N₂, (rather than the reaction between NO and CO). This occurs through a series of reactions, three of which are summarised below:



Where the atoms in parenthesis represent atoms bound in the carbon soot layer. The reduction of NO to N₂ in the fizz zone is highly exothermic, which thereby increases the burn rate. Some further evidence can be found for the reaction between NO and carbon in the work of Lengellé [18], where detection of NO and C can be found near the burning surface of unmodified propellants. Furthermore, addition of carbon black to DBPs is observed to have a small increase on the burn rate [18,29].

After the formation of carbon deposits, Youfang [36] postulated that PbO presents a secondary process in the combustion of carbon:



Evidence for this has been observed in the formation of lead droplets on the carbon surface [10,28]. Moreover, Sharma et al. found that soot contained both lead and lead oxide through Auger electron spectra [44]. Pressure influen-

ces the amount and the covering ratio of soot by the conductive heat feedback in the fizz zone. As the pressure rises, the conductive heat feedback increases, increasing the temperature at the burning surface, as was also shown by Kubota et al. [9,29], (see Figure 7). As the pressure rises further, reactions (9) and (11) become more dominant, diminishing the carbon soot layer, which eventually leads to plateau/mesa burning. Of interest is the results of Sharma et al. [44], who found that lead oxide dominates over Pb at higher pressures, which concurs with the loss of carbonaceous layer with lead particles on top, leaving PbO particles behind. However, they could not distinguish between different forms of lead oxide.

Overall, the carbon theory states that the basic burning process of DBP involves the formation of a limited amount of carbon in the condensed phase, which increases in the presence of lead salts. The formation of the carbon matrix catalyses the reaction involving the reduction of NO to N₂ [10,36]. As these reactions are exothermic this will lead to a higher temperature, thereby accounting for a higher burning rate. The reaction between the carbon-lead complex (be that Pb/C [10,29] or PbO/C [21,36]) and NO occurs in the fizz zone near the burning surface. According to Singh and Rao [30], the catalytic effect, and it's the subsequent loss, is dependent on the C/NO ratio in the fizz zone as given below:

$$\text{C/NO} > 1, \text{ super - rate burning} \quad (13)$$

$$\text{C/NO} \approx 1, \text{ plateau effect} \quad (14)$$

$$\text{C/NO} < 1, \text{ mesa effect} \quad (15)$$

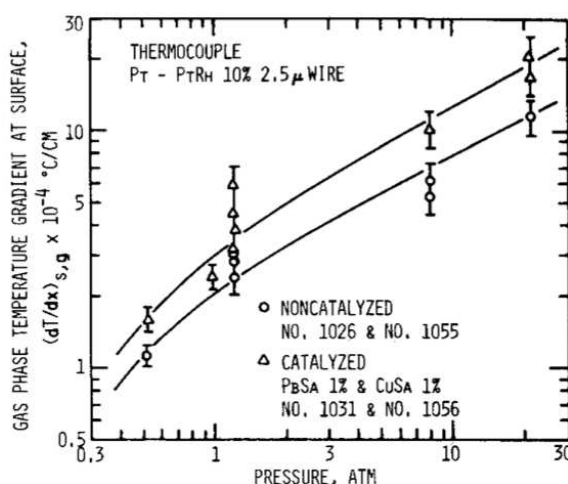


Figure 7. Gas phase temperature gradient at burning surface showing higher rate of heat feedback from fizz zone to solid phase zone when propellant is catalysed [9]. Copyright (1984) American Institute of Aeronautics and Astronautics.

These calculations are based on conversion of carbon to CO and nitrogen to NO in the fizz zone, and 50% conversion of hydrogen to H₂O. They also support the effects of carbon black on the mechanism of burning in DBPs, where too much carbon black (*i.e.* C/NO ratio above unity) only results in super-rate burning [30].

The carbon soot theory is by far the most coherent in terms of providing a super-rate effect explanation, although the dispute around whether Pb or Pb-based compounds serves as the actual catalyst remains to be further investigated. Moreover, whether carbon soot can act as a catalyst to promote NO reduction still needs to be confirmed.

Free radical theory. According to Sinha et al. [38], lead salts transport short lived free radicals like CH₃[•] and C₂H₅[•] as lead-alkyls from the burning surface to the fizz zone, whereupon they decompose into metal lead and free radicals. A chain reaction then takes place between NO and free radicals, resulting in the fizz zone becoming hotter. This results in more heat transfer to the propellant surface, thereby increasing the burning rate. As the pressure increases, the free radicals are removed due to increased collision rates, resulting in the plateau region. The formation of gaseous Pb atoms in the fizz zone corresponds with the photochemical and chelate theories, moreover, Farber et al. [28] detected gaseous Pb atoms in their mass spec investigations. Kubota et al. [29] also agree that conductive heat feedback from the fizz zone to the burning surface results in super-rate burning. However, the review by Rao and Singh pointed out that a series of metals would all react to produce metal alkyls, but no plateau burning ensues [45].

Current Trends Towards Ballistic Modifiers in Double Base Propellants

As introduced earlier in this review, the most effective form of ballistic modifier in DBPs is the addition of lead salts in combination with copper oxide and solid carbon material [18]. Recent trends in the energetic materials field include the application of carbon material into two groups: nano-powdered carbon, such as carbon black and nano-diamond, form one group, while carbon nanomaterials (CNM), such as carbon nanotubes (CNTs), graphene and graphene oxides (GOs), form another. Both groups offer the advantages of large surface areas and strong gas adsorption capacities. The latter group [46,47] is further valued due to their enhanced mechanical properties, which includes insensitivity to friction [46,47], and their chemical flexibility, as functional groups can be added to the surface of GOs; a review paper on the topic of functional CNMs within the energetics field was published in 2015 [48]. In particular, the inclusion of graphene and GOs has been used successfully to deposit a diverse range of energetic materials onto the nano-carbon surface [49–52], including with NC [53] for DBP applications. The burn rate for NC increased in the presence of GO, forming GO/NC films of a porous nature,

such that the GO acted in the role of both catalyst and carrier. However, it is still the addition of lead salts to these systems that results in the formation of plateau/mesa burning in DBPs.

Effects of nano-sized burn-rate catalysts. Much of the work on catalytic combustion with nano-sized burn-rate catalysts for DBPs has been performed by Zhao et al. [54–58], and an extensive review of this work can be found elsewhere [59]. Initial investigations have focused on nano-metal oxides (without CNM surfaces) including nano-Bi₂O₃, nano-CeO₂, nano-Cu₂O, nano-NiO, and nano-PbO [56]. The smallest pressure exponent for these catalysts is observed for nano-PbO, with $n = 0.268$ in the 6–12 MPa pressure range. Likewise, for their macro metal oxides, nano-Bi₂O₃, nano-CuO and nano-SnO₂ have some catalytic effect on the burning rate, but fail to produce plateau combustion [56]. On the other hand, nano-CeO₂ and nano-NiO decreased the burning rate with increasing pressure, producing no super-rate burning, and so cannot be considered as burn-rate catalysts. A series of binary metal oxides, namely nano-PbO–CuO, nano-CuO–SnO₂, nano-MgO–SnO₂ and nano-CuO–Cr₂O₃ were also studied. All failed to produce plateau burning with the exception of the combined PbO and CuO system, which produced mesa burning at 4–6 MPa; this behaviour likely mirrors the effect observed for the parent single metal oxide components. However a further paper by Zhao et al. on nano Bi₂WO₆ did successfully produce a very low pressure exponent in the high pressure range of 16–22 MPa (n is 0.11 at 22 MPa, see Figure 8), and thus provides the first potential lead for a Pb-free burn rate catalyst [54]. However, this plateau burning is at a much higher pressure than nano-PbO (6–12 MPa), and may limit its use within DBPs.

Effects of nanothermites as burn-rate catalysts. Nanothermites are an energetic material composed of metal fuel, typically nano-Al, and a nano-metal oxide oxidiser such as CuO, MoO₃, Fe₂O₃, WO₃, PbO and Bi₂O₃ [59–63]. Within their application as ballistic modifiers in DBPs, nano-Al/CuO, nano-Al/PbO and nano-al/Bi₂O₃ and their binary combinations have been studied by Zhao et al. [59,61,64,65]. The unique dominance of nano-Al/PbO as a burn-rate catalyst over nano-Al/CuO and nano-Al/Bi₂O₃ is again observed, with increased super-rate burning at low pressures observed. The increase in catalysis at low pressures is greater than that observed for nano-PbO alone, and pressure exponents are somewhat reduced in the 8–14 MPa pressure range. However, the synergistic combination of nano-PbO and CuO previously observed to produce mesa-burning does not act as a ballistic modifier when complexed with Al in DBPs [48].

Effects of nano-sized burn-rate catalysts supported on CNMs. Nanoparticles of burn-rate catalysts, dispersed over the CNM surface have also been investigated [66,67]. It has been shown that the use of CNMs in a carrier capacity can prevent the aggregation of nanoparticles, thereby improving their catalytic efficiency [68,69]. Using carbon nano-

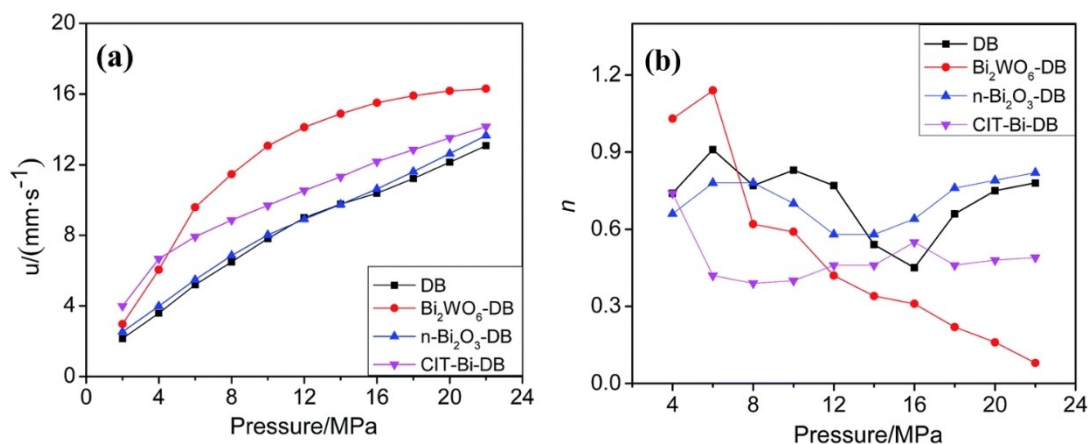


Figure 8. (a) Burning rate curves and (b) pressure exponents of different double base (DB) propellants, in the presence of nano Bi_2WO_6 , nano- Bi_2O_3 and bismuth citrate (CIT) burn rate catalysts [54]. Copyright Royal Society of Chemistry 2015.

tubes (CNTs) as a carrier, a variety of nanoparticle catalysts have been tested, including Pb, CuO, Bi_2O_3 and NiPb [68–70]. None of these materials sustained plateau burning, although super-rate burning and a decrease in the pressure exponent at much higher pressures (16–22 MPa) was observed. An important invention in this field is the use of a Cu–Bi/CNT catalyst on DBPs, which produced super-rate burning at 2–8 MPa, and a low pressure index ($n=0.173$) in the 10–22 MPa pressure range (Figure 9). This pressure range is lower than that of nano- Bi_2WO_6 but still higher than the low pressure plateau regime of nano PbO at 6–12 MPa. This is the first known Pb-free bi-metallic ballistic modifier in DBPs to produce plateau burning [71], but its mode of action is currently unknown.

In addition to the use of carbon nanotubes, graphene oxides lend themselves as carriers of nanoparticle burn-rate catalysts. Much work has focused on the aforementioned copper, bismuth, lead and tin oxide materials (and their binary combinations) [57]. To summarise this work, PbO and

nano-PbO based GOs were found to produce a burn-rate enhancement at low pressures, and plateau burning at 6–14 MPa [57]. Notably, the mesa burning effect (at 12–20 MPa) was produced when nano-PbO was incorporated with nano- Cu_2O and GO [57], suggesting similar behaviour to the traditional Pb-based ballistic modifier behaviour. Nano- Bi_2WO_6 has also been deposited on GO, and a catalytic effect demonstrated, but no burn-rate behaviour on DBPs has yet been reported [72].

Energetic ballistic modifiers. Another trend in the work of Zhao et al. has been the introduction of energetic functionality to ballistic modifiers in order to increase the combustion rate of the system. These take the form of anthraquinone salts containing metal ions (Pb/Cu), and hydroxyl and nitro groups [73]. These catalysts provide much better modification of the plateau region towards medium gas pressures, as quantified by very low pressure exponents. However, the authors were unsure whether the lead salts would decompose into Pb radicals or PbO. While they did discuss the formation of elemental carbon from the organic part of the salt, no experimental evidence was provided.

To summarise, the recent trends in burn rate modifiers for DBPs have focused on the incorporation of carbon nanomaterials into energetic formulations. The most effective CNMs in this field take the form of graphene oxides (GOs), which have large surface areas, some catalytic capacity, and the ability to disperse nanoparticles of burn rate catalyst, thereby preventing agglomeration. This effect has seen an increase in catalytic activity for all previously used ballistic modifiers, in particular PbO, CuO and Bi_2O_3 . And while the most effective burn rate modifier remains the combination of lead oxide with copper oxide and carbon [18,57,59], new directions in binary combinations of metals provide Bi_2WO_6 nanoparticles [54] and Cu–Bi/CNT catalysts [71] at the forefront of other avenues of research are worthy of further endeavour.

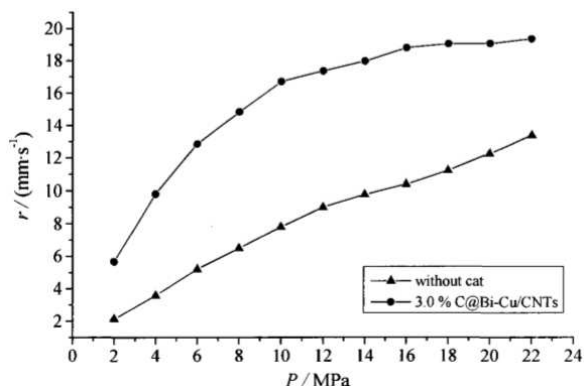


Figure 9. Burning rate curves of double base propellants (DBPs), in the presence of a carbon-film, coated Cu–Bi/ carbon nanotube (CNT) catalyst. Copyright Patent N101757927B [71].

Conclusion

Plateau or mesa burning rates are essential characteristics of propellant materials as they create combustion conditions that produce thrust that is insensitive toward changes in chamber pressure over a desired range, thereby enhancing control and reliability in their use. Currently, lead-based ballistic modifiers offer the best attributes to control the burn rate of nitrate ester propellants, but incoming European legislation will soon outlaw their use. There is, therefore, an urgent need to replace lead with other ballistic modifiers that can still produce mesa- or plateau-burning regions in DBPs but will at the same time be free from toxicity concerns. However, as current attempts to replace lead with another element have met with only partial success, there is now a need to understand at a more fundamental level how lead-based ballistic modifiers produce super-rate and plateau burning, in order to obtain the key characteristics required of any potential replacement material.

This review has highlighted that most of the fundamental work done in this field dates from 1950s–1990s. Of the four theories reviewed, the photochemical theory can largely be dismissed by the available experimental data. The other three theories offer consensus on the site of action of lead catalysis in combustion flames. They suggest that the site of catalytic action is in the condensed phase foam zone and/or in the fizz zone just above the burning surface. There is little evidence for catalysis in the dark zone or secondary flame zone. Of the theories, the carbon soot theory is the most coherent and provides the most correlation with experimental evidence. The lead catalyst is proposed to have two roles; the first is to promote the formation of carbonaceous matter in the condensed phase, the second is to facilitate the fizz zone reactions, either in the increased reduction of NO to N₂ or in the increased oxidation of the carbonaceous layer to CO₂. The acceleration of these exothermic reactions increases the burn rates and account for super rate burning. The disappearance of the lead-carbon matrix accounts for the plateau/mesa burning. In this way, the carbon soot theory is the only theory which accounts for mesa and plateau burning. However, it is not clear whether the role of the catalyst is in the form of lead, lead oxide or carbon or a combination of the three.

Finally, the work of the last twenty years has highlighted a role for functional carbon nano-, materials, such as graphene oxides, dispersed with nanoparticles (PbO, Cu₂O, Bi₂O₃ etc) which offer new avenues to alter the combustion rate behaviour of DBPs and other energetic materials. While super-rate burning has been observed for these additives, no evidence was obtained to support plateau/mesa-rate burning. The two known exceptions to this is nano-Bi₂WO₆ and Cu/Bi encapsulated in carbon nanotubes, but currently, a fundamental understanding into their reaction mechanisms is unknown. As a promising avenue towards deliver-

ing lead-free ballistic modifiers for DBPs, we hope that this work will shortly be forthcoming.

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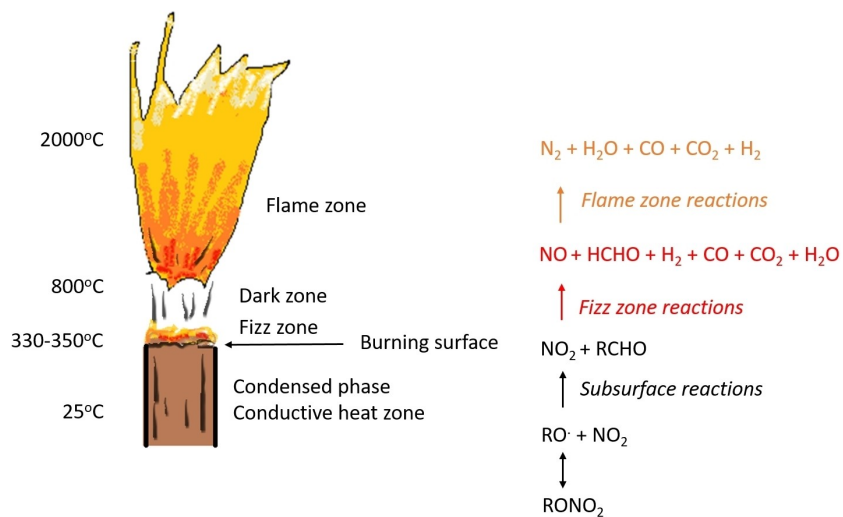
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REVIEW



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